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## SOLUBILITY OF FINELY DISPERSED POWDERS OF CALCIUM-CONTAINING GLASSES IN A WATER MEDIUM. CALCIUM-SILICATE GLASSES

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The effect of the composition of calcium-silicate glasses on the behavior of powders with different dispersity (500, 60, and 10  $\mu\text{m}$ ) in a water medium is investigated. The acid-base characteristics of the water medium and the concentration of calcium ions in a water solution after soaking glass powders are determined. It is shown that the main parameter determining the mechanism of the glass dissolution in water is their basicity modulus.

Modern stomatological composite photo- and chemical-hardening filling materials which are used to fill cavities and restore teeth must meet an entire series of requirements, including the no negative (allergic, toxicological, and so forth) effects on the body and preservation of a neutral pH in the mouth. The next-generation composite materials contain neutral polymer acrylic matrices and different filling materials, such as glass and amorphous and crystalline silica [1, 2], whose purpose is to decrease the polymerization shrinkage of a filling as the filling hardens.

It is known that the pH in the mouth varies in the course of a day from slightly alkaline to slightly acidic. Deviations from the normal regime can cause degradation of the enamel and dentine of healthy teeth as well as increase the size of the cavities containing the filling material and make it necessary to fill the cavity. To stabilize the reaction of the medium in the cavity of the tooth and strengthen the dental tissue, a calcium-containing compound is introduced into the composite filling material. Calcium-containing glasses, which possess high transparency and do not degrade the aesthetics of the filling composites, are undoubtedly of interest for use in filling material.

For our investigations we chose silicate glasses with a high content of calcium, which, according to the results of a determination of the chemical stability, engender a slightly alkaline reaction in a water medium. When the composite materials are synthesized, the filler is introduced in the form of finely dispersed powders with particle size ranging from 0.1 to 10.0  $\mu\text{m}$ , while particle size determined on the basis of chemical stability was 500–800  $\mu\text{m}$ . At the same time it is

known that as the specific surface area of the powder increases, the dissolution of the powder intensifies and the characteristics of the water medium can change. In this connection, a comparative investigation was performed of the influence of the composition of glasses on the behavior of powders with different dispersity (500, 60, and 10  $\mu\text{m}$ ) with a long holding time in the water medium. The characteristics of calcium-silicate glasses are presented in Table 1.

The glass powders were obtained by multistage grinding: to particle size 500  $\mu\text{m}$  — in an Abbich mortar, 60  $\mu\text{m}$  — in a MK-60 disk abrader, and 1–10  $\mu\text{m}$  — in alcohol in a “Fritch” mill for 10 h. The milling bodies were 8 and 12 mm in diameter agate balls. The specific surface area of the glass powders was determined with a PSKh-2 analytical apparatus.

After the chemical stability was determined by the boiling method, the following regimes of thermostating of glass powders in a water medium at 36.5°C were used:

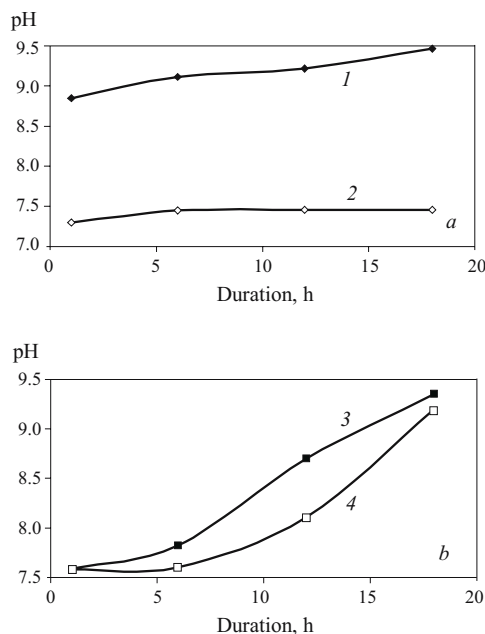
first regime) holding times 1, 6, 12, 18, 24, 48, and 72 h, glass powder : water ratio 1 : 100;

TABLE 1.

Glass	Molar content of the main components, %		Basicity modulus	pH after chemical stability determination
	SiO <sub>2</sub>	CaO		
1-2A	40.0	54.0	1.35	7.8
1-3A	45.0	49.0	1.09	7.6
1-4A	50.0	44.0	0.88	7.4
1-5A	55.0	39.0	0.71	7.2

\* The Al<sub>2</sub>O<sub>3</sub> content was 6.0% in all cases.

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**Fig. 1.** Influence of the composition and thermostating time of glass powders on the acid-base characteristics of the water medium; the average size of the glass powder particles is 60  $\mu\text{m}$  (a) and 10  $\mu\text{m}$  (b): 1) composition 1-2A, basicity modulus 1.4; 2) composition 1-5A, basicity modulus 0.7; 3) composition 1-3A, basicity modulus 1.1; 4) composition 1-4A, basicity modulus 0.9.

second regime) the water phase changed every 1, 3, 7, 14, 28, and 32 days, which corresponds to the rate of fluid turnover in the body; the glass powder : water ratio is 1 : 10 (SERIC UN-8 thermostat, procedure developed at the All-Russia Scientific – Research and Testing Institute for Medical Technology).

The pH of the solutions obtained and the concentration of the calcium ions were determined with an I-160M universal ionometer [3].

When the chemical stability of a calcium – silicate glass is determined (see Table 1), the pH of the water is observed to increase gradually from 7.2 to 7.8 and the basicity modulus of the glass increases from 0.7 to 1.4. This behavior is due to the disordering of the glass structure as a result of a decrease of the glass-forming silicon oxide content in it and

the formation of a chain structure instead of a frame structure; this has been confirmed by investigations of the structure of the glasses by IR absorption spectroscopy (Table 2). Increasing the content of the quite mobile calcium cations in the glass increases the concentration of these cations in water and results in a weakly alkaline reaction of the water medium instead of a neutral reaction.

The influence of the basicity modulus becomes sharper when calcium – silicate glass powders are thermostated according to the first regime. Figure 1a displays the pH versus the thermostating time of glass powders with 60  $\mu\text{m}$  particles and basicity modulus 0.7 and 1.4. It is evident that as the particle size decreases by an order of magnitude (from 500 to 60  $\mu\text{m}$ ) the pH of the water medium differs by more than one unit after glass powders with different basicity modulus are allowed to stand in it and this difference increases with the thermostating time. The character of the curves attests to a high resistance of glass with basicity 0.7 to water (the pH fluctuations are 0.1 – 0.2) and a gradual increase of the dissolution rate for high-calcium glass with basicity 1.4 (pH increasing by 0.6). It is obvious that the first glass essentially does not release any calcium ions into the solution and cannot serve as a donor of such ions in the filling material, while for the second glass the rate of release of calcium ions into solution is characteristically high, which can have a negative effect on the stability of the medium in the cavity of the tooth in the presence of such a filling material.

Glasses with basicity modulus 0.9 and 1.1 were used for subsequent tests.

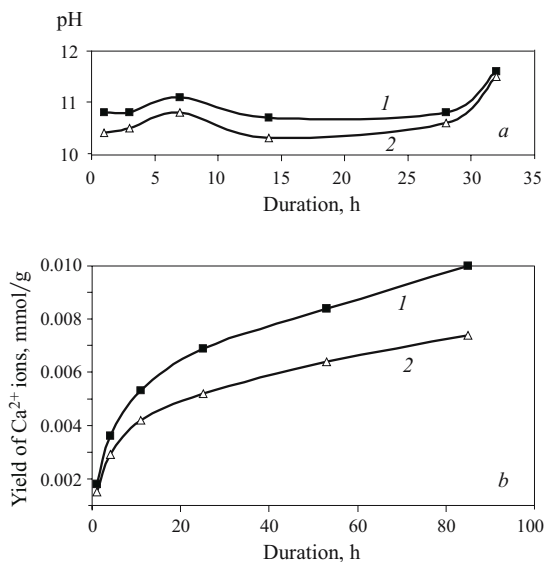
During thermostating of glass powders with basicity modulus 0.9 and 1.1 and particle size 10  $\mu\text{m}$  in the first regime, the pH gradually increases from 7.6 to 9.5 as the holding time increases (Fig. 1b). In the second thermostating regime the pH of the water medium fluctuates over the range 10.5 – 11.5 during the entire period of the investigations and the concentration of calcium ions and solution fluctuates in the range 0.001 – 0.002 mmol/g (Fig. 2a). However, the total release of calcium ions from the glass gradually increases and, as shown in Fig. 2b, is about 0.01 mmol/g after 83 days.

The substantial difference of the pH of the water medium between the thermostating regimes is due to, first and foremost, the change in the ratio glass powder : water from 1 : 100 to 1 : 10. Thus, the concentration of calcium ions in the solutions obtained with thermostating in a regime with a change of the water phase, when on completion of the process a fresh portion of water is poured onto the glass powders, should be approximately an order of magnitude higher than for thermostating in the first regime. Unfortunately, it is impossible to evaluate this quantitatively because of the low concentration of calcium ions in the solutions after glass powders are thermostated in the first regime.

The stability of the pH of the water medium in a regime with a change of the water phase, the negligible fluctuations of the concentration of the calcium ions in each portion of the solution, and the gradual increase of their migration out

**TABLE 2.**

Composition	Basicity modulus (CaO : SiO <sub>2</sub> )	Si – O – Si absorption band, cm <sup>-1</sup>	Main structural motif
1-2A	1.4	1000, 900	Island combined with [SiO <sub>4</sub> ] chain
1-3A	1.1	1000	[Si <sub>2</sub> O <sub>7</sub> ] <sub>n</sub> chain (metasilicate)
1-4A	0.9	1050	[Si <sub>2</sub> O <sub>7</sub> ] <sub>n</sub> layered (disilicate)
1-5A	0.7	1080	[SiO <sub>4</sub> ] <sub>n</sub> frame



**Fig. 2.** Influence of the thermostating time of glass powders on the acid-base characteristics of the water medium (a) and the yield of calcium ions (b): 1 and 2) compositions 1-3A and 1-4A, respectively.

of the glass powder under study show that the calcium ions diffuse out of the glass at a constant rate. Many investigations of the behavior of silicate glasses containing alkali and alkali-earth oxides in water solutions have shown that three regions can be identified in the surface layer of the glass during the dissolution process [4].

The first region, which lies on the glass – water boundary, is called the leached, zero-gradient, or gel layer, since the concentration of the modifying cation is negligibly low in it. The thickness of this layer is determined by the mobility of the modifying cation in the glass and the rate of diffusion of this ion into the water medium. The fact that the concentration of the cation in the medium remains constant as the holding period increases attests to the presence of the leached layer.

The second region connects to the leached layer with a layer where the initial main composition of the glass is preserved and is called the gradient or transitional layer. This layer is characterized by a composition gradient due to an increase in the concentration of the modifiers present in it and by a decrease of their migration with decreasing distance from the surface of contact with water. The amount of the modifying cation diffusing out of this layer gradually decreases as the thermostating time increases.

Finally, the third region is the main composition of the glass proper, where the content of components and structural parameters are not subject to external effects.

The values obtained for the pH and the concentration of calcium ions as a function of the thermostating time of calcium – silicate glasses suggest that the leached layer forms quite rapidly on the surface glass with basicity modulus 0.7 — approximately after 6 h of thermostating; in addition, as the dissolution time increases, the thickness of the leached layer (silicic acid gel) and the rate of diffusion of calcium ions through it limit the dissolution process.

As the basicity modulus of calcium – silicate glasses increases (0.9, 1.1, and 1.4), the thickness and the role of the leached layer in the dissolution process decrease. It is evident from the curves presented in Fig. 1 that after the glasses are thermostated the alkalinity of the media increases and at the same time their basicity modulus and the calcium oxide content in the glass increase. The shape of the curves of the calcium ion concentration versus the thermostating time (see Fig. 2b) attests to the fact that a gradient layer is present and is different thickness in glasses with basicity modulus 0.9 and 1.1.

The investigation of the behavior of calcium – silicate glass powders in a water medium has shown that the main parameter responsible for the sequence of processes occurring during dissolution is their composition, which is characterized by their basicity modulus. The dispersity of the powder influences only the concentration of the modifying cation in the water medium. Thus, when glass powders with particle size greater than 60  $\mu\text{m}$  were thermostated for one day the concentration of calcium ions in the water medium was less than  $10^{-5}$  mmol/g, while for powders with 10  $\mu\text{m}$  particles studied under the same conditions the concentration of calcium ions in the water medium was 0.001 – 0.002 mmol/g.

The character of the change of the parameters of the water medium in the presence of calcium – silicate glasses with basicity modulus close to 1 shows that these glasses can be recommended as calcium-releasing fillers for photo- and chemically hardened stomatological matrices.

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